NEAR INFRARED SPECTROSCOPY FOR ON-LINE ANALYSIS OF ALKYLATION PROCESS ACIDS

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INTRODUCTION

Alkylate, formed by the acid-catalyzed reaction of isobutane with C3-C5 olefins, is a key component for motor fuel blending. In the United States, current production is about 1×10^6 bbl/day, and represents 11-15% of the gasoline pool (somewhat higher in California).[1] Alkylate is comprised essentially of highly branched isoparaffins and has very high octane values, often in the 94-97 range for RON. It has low vapor pressure, narrow distillation range, and is essentially devoid of olefins, aromatics, and sulfur, making it the preferred blending component for reformulated gasolines (RFG). The demand for alkylate in the US is expected to lead to capacity expansions of 10-35%.[2]

HF alkylation is an important and widely-used process for making high-quality alkylate. Although the HF process has been used around the world for >50 years, efforts to optimize individual unit performance are always underway. Optimization can lead to significant economic advantage, since US capacity utilization is already 90%.[2]

The generally recognized advantages of on-line process monitoring, such as tighter process control, higher productivity, and improved product quality has led to much recent interest in this area. Continuous and immediate feedback of quantitative information is critical for optimized operation. These features are ideally suited for the alkylation process, where changes in the acid composition can occur more rapidly than can be observed with samples taken at normal intervals. Acid composition is important for optimal product quality, but until recently no on-line method existed for the determination of total acid composition.[3,4] Acid, water, and acid-soluble oil (ASO) concentrations are usually determined on intermittent samples taken to a laboratory. We have recently demonstrated the feasibility of using Near Infrared (NIR) spectroscopy for the on-line determination of HF, water, and ASO,[3] and here report application of those methods under continuous alkylation conditions.

EXPERIMENTAL

The laboratory scale alkylation unit used in this work has been described previously.[3] The unit consists of a riser reactor, feed dispersion device, acid settler, acid recirculation pump, and product collection equipment.

The NIR data were collected with a flow cell mounted between the acid heat exchanger and acid pump; all of the acid inventory flows through the cell during each pass around the reactor. The cell was constructed of Hastelloy C alloy, using sapphire windows. For each run, a pre-blended feed of olefins and isobutane was introduced to the reactor.

Starting acid was 98% HF and 2% water by weight. The acid/hydrocarbon emulsion from the reactor is routed to the settler, where the acid phases out to the bottom and is recirculated to the reactor. Product hydrocarbon is withdrawn from the top of the settler, scrubbed to remove any HF, and collected for analysis. Acid samples were withdrawn intermittently for HF and ASO determination to provide a comparison for NIR values. All spectral data were collected using an Applied Automation Advance FT-IR. The instrument was coupled to the cell using 600 μm low-OH silica optical fiber. The data were processed using a partial least squares model developed from a calibration dataset described earlier.[3]

RESULTS AND DISCUSSION

Selected results for Run #1 are given in Table 1. The feed was a blend of refinery-supplied olefins and isobutane, and a feed introduction device was chosen in order to increase the amount of ASO produced over that normally observed. This allowed enough ASO to be generated for a good comparison between NIR and standard techniques.

Standard HF titrations (dilution and titration to phenolpthalein endpoint) gave values within 2-3 wt% of the NIR values. The ASO concentrations determined by extraction (after neutralization) were usually only 50-70% of the NIR values. This was expected because the NIR measures total ASO, while the extraction measures mostly heavier ASO (*vide infra*). Water was not analyzed by an independent method; however the concentrations determined by NIR varied within a fairly narrow range (1.8 and 2.2 wt%). Figure 1 shows the trend lines associated with HF, ASO, and water at increasing times on stream.

After 92 hours, the feed was spiked with 570 ppm MTBE (or ~7000 ppm based on olefin only). MTBE is commonly produced upstream of the alkylation unit as an oxygenate for RFG. Under normal operation the concentration of MTBE in the alkylation feed is nil, but under upset conditions, levels of 1000-5000 ppm can have rapid, deleterious consequences for acid purity due to accelerated ASO production. Table 2 gives the results for the acid analysis at selected times on stream. Again the HF values from NIR are within 1-2 wt% of the titration values. Note the 70% increase in ASO concentration between 92 hours (table 1) and 113 hours (table 2), reflecting the high propensity for ASO production from MTBE. The increase in ASO based on traditional data was only ~33%. Both the NIR and traditional data show an increase in ASO with time, but again with traditional tests we observed only ~50-65% of the total ASO determined by NIR. Water remained relatively constant until purity was increased after 167 hours. At this time, the catalyst was nearly deactivated, necessitating a reduction of ASO and water and an increase in HF concentration. Figure 2 shows the trend lines for HF, ASO, and water with the MTBE-containing feeds.

One of the key advantages of NIR is the fast response time; in the present work spectra were taken every six minutes (times as short as 1 minute are possible). The inherent precision of NIR is another significant advantage, showing a 30- to 50- fold improvement in repeatability when compared to the traditional laboratory test methods for HF, water, and ASO. The current technique allows the rapid determination of HF, ASO, and water *directly* and *independently* of each other, in the presence of other dissolved/dispersed non-ASO hydrocarbons (C3, iC4, nC4, C5+ alkylate, etc.). This is a result of the method in which the training set data was collected. The NIR results add to 94% since the raw data was normalized to reflect the usual rule of 6% hydrocarbon dissolved/dispersed in the acid phase. In all cases, the sum of the raw data for HF, ASO, and water was between 99.6 and 100.1%, even though the model was *not* constrained to give that result. In traditional analyses, the difference between 94% and the sum of the acid components is taken as an indication of light ASO. As these data show, the traditional tests gave an indication of ~1-3% light ASO (the titration value of 93% at 44 hours is likely an outlier). The NIR technique is set up (by design) to measure both light and heavy ASO. This is the reason for the discrepancy between NIR and extraction measurements. Lighter ASO components are frequently lost during sample preparation for traditional tests.

The "spikes" present in Figures 1 and 2 occurred when acid was either added to or withdrawn from the reactor. These spikes in the trend lines result from the formation of gas/vapor bubbles which form inside the cell. Nitrogen is used as a pressure source for acid addition and to maintain constant unit pressure. As acid is withdrawn or added, a pressure differential results. The cell, which is located between the acid cooler and the magnetically driven acid recirculation gear pump, is susceptible to N2 gas bubble formation in the acid line. If bubbles develop, they can easily be trapped in the cell, since all of the acid in the system is routed through the cell. The gas bubbles cause rapid changes in the optical pathlength, resulting in wildly fluctuating values. The bubbles could be removed from the system by manipulation of the acid flow rate. Gas/vapor bubble formation is a phenomenon related to the experimental set-up in the laboratory, and proprietary equipment has been designed to eliminate their formation.

CONCLUSIONS
NIR appears to be ideally suited for on-line analysis of circulating acid in alkylation units. The fast response times, improved repeatability, and ability to provide quantitative information on HF, ASO, and water directly and independently in circulating acid represents a significant improvement over traditional methods of analysis.

REFERENCES
1. Rao, P., Vatcha, S.R., *Oil & Gas Journal*, 94(*37*), 56 (1996).

2. Rhodes, A., *Oil & Gas Journal*, 92(34), 49 (1994).

3. Heald, R.L., Randolph, B.B., Eastman, A.D., "NPRA National Meeting", March 16-18, 1997, San Antonio, TX, paper AM-97-57.

4. Ramamoorthy, P., US Patent 5,681,749, October 28, 1997.

Table 1. NIR and Traditional Acid Test Results: MTBE-Free Feed

TOS (Hours)	20	44	68	92
%HF (titration)	89.3	93.0	86.6	88.4
%ASO (extn)	0.85	1.25	2.09	2.52
%H2O (NIR)	1.80	2.0	2.19	2.16
TOTAL	92.0	96.3	90.9	93.0
%HF (NIR)	91.81	90.22	88.69	88.02
%ASO (NIR)	0.391	1.78	3.12	3.92
%H2O (NIR)	1.80	2.00	2.19	2.06
TOTAL	94.0	94.0	94.0	94.0

Table 2. NIR and Traditional Acid Test Results: 570 ppm MTBE In Feed

TOS (Hours)	113	143	167	191
%HF (titration)	87.3	86.4	84.2	86.0
%ASO (extn)	3.35	4.0	4.7	4.7
%H2O (NIR)	2.01	2.08	2.01	1.78
TOTAL	92.7	92.5	90.9	92.5
%HF (NIR)	85.3	84.4	83.3	85.0
%ASO (NIR)	6.71	7.51	8.73	7.28
%H2O (NIR)	2.01	2.08	2.01	1.78
TOTAL	94.0	94.0	94.0	94.0